

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
29 August 2002 (29.08.2002)

PCT

(10) International Publication Number
WO 02/066372 A1

- (51) International Patent Classification⁷: **C01B 13/18**
- (21) International Application Number: **PCT/BR01/00020**
- (22) International Filing Date: 19 February 2001 (19.02.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (71) Applicant (*for all designated States except US*): **FUNDAÇÃO DE AMPARO À PESQUISA DO ESTADO DE SÃO PAULO** [BR/BR]; Rua Pio XI, 1500, Alto de Lapa, CEP-05468-901 São Paulo, SP (BR).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **DE SOUZA, Milton, Ferreira** [BR/BR]; Rua Alberto Lanzoni, 740, CEP-13562-390 São Carlos, SP (BR). **DOS SANTOS BATISTA, Paulo** [BR/BR]; Alameda das Azaleias, 335, CEP-13566-500 São Carlos, SP (BR). **LIBORIO, Jefferson, Benedicto, Libardi** [BR/BR]; Rua Ana Prado, 926, CEP-13574-000 São Carlos, SP (BR).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— *with international search report*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: OXIDES EXTRACTED FROM VEGETAL MATTER AND PROCESS THEREFOR

(57) Abstract: The invention concerns a process for the extraction of acid or basic oxides contained in a vegetal matter, more specifically it concerns the extraction of silica from rice husks. The invention also concerns pure oxides extracted from vegetal matter. The invention also concerns the process for the extraction of carbon-rich oxide compositions from vegetal matter, and compositions obtained through said process.

WO 02/066372 A1

OXIDES EXTRACTED FROM VEGETAL MATTER AND PROCESS THEREFOR.

The present invention concerns pure oxides (acid or basic oxides) extracted from vegetal matter, as well as carbon-rich oxide compositions
5 extracted from vegetal matter. Another aspect of the invention concerns a process for the extraction of oxides contained in vegetal matter; more specifically it provides a process for the extraction of silica from rice husks or from the rice plant.

The description that follows makes reference to a preferred
10 embodiment of the invention, namely the extraction of silica from rice husks. This is done simply to favor the understanding of the invention, without imposing any limitation to the scope of the invention, defined in the attached claims.

Amorphous silica, SiO_2 , under its non-crystalline form, is a substance
15 that has many uses. Its commercial value is strongly tied to its purity, specific area and particle size. Particles between 10 and 1000 nm (nanometers) are known as nanoparticles, and due to their small radius have high chemical reactivity and sinterization capacity.

Among the known processes for obtaining amorphous silica are the
20 reaction between silicon monoxide, SiO and oxygen, and the mere burning of rice husks by the grain companies. This last case leads to a product known as rice husk ash.

The ash from the burning of rice husks contains high content of black carbon, about 60% by weight of silica, and some impurities mainly
25 potassium, sodium, magnesium and calcium. The elimination of the carbon from this mixture to obtain high purity silica requires the use of high temperatures, a procedure that leads to BET specific areas of about $10\text{m}^2/\text{g}$ and average particle size above $50\mu\text{m}$. The dry rice husk mass corresponds

to about 20% of the *in natura* grain, a variable value according to the plant variety, the climate, and agricultural procedures employed with the plant culture.

5 Rice husks comprise mainly cellulose, lignin, hemicellulose, silica and other inorganic oxides, these last ones representing about 4.5% of the silica mass, potassium and calcium having the highest content.. Such values depend on the plant variety, climate and rain distribution.

Known in the state of the art is a process for the extraction of silica from rice husk developed by Real et. ali. (*C. Real, M.D. Alcalá and J. M. Criado, "Preparation of Silica from Rice Husks" J. Am. Ceram. Soc. 79 [8] 2012-12 (1996)*). Such a process consists of boiling the rice husks for two hours in a 10% hydrochloric acid distilled water solution , under ambient pressure, at a temperature of no more than 100°C. The husks are then washed with distilled water to eliminate salts and compounds of potassium,
15 sodium, calcium and magnesium that contribute to the later aggregation of particles of amorphous silica during calcination. Calcination at 600°C follows, during an unknown amount of time, resulting in a white, amorphous and free from carbon silica, with a low content of other inorganic compounds, specific area of 260 m²/g, a non specified particle size,
20 but found to be between 15 and 20 µm by the inventors of the present invention.

The present invention has as an object an efficient, simple and cheap industrial process for extracting the oxides contained in vegetal matters. In a preferred embodiment, the process refers to the extraction
25 of acid oxides.

Another object of the invention are carbon-rich oxide compositions extracted from vegetal matters. Still another object of the invention are highly pure oxides extracted from vegetal matters.

These and other objects of the present invention are better understood by means of the text and examples that follow, the scope of the invention being limited only by the content of the claims appended hereto.

5 The process of the present invention comprises some or all of the following steps:

A. Hydrolysis of the vegetal matter (acid hydrolysis for the extraction of acid oxides, basic hydrolysis for the extraction of basic oxides), at a temperature above 100°C, under pressure;

10 B. Washing/drying

C. Fragilization of the structure;

D. Disaggregation of the structure;

E. Calcination;

F. Milling

15 More details are now presented, concerning a preferred embodiment of the invention, not in any way limiting the scope of the invention. It concerns the process for the extraction of silica from rice husks, as well as carbon-rich oxide compositions and pure silica extracted from vegetal matter.

20 A. Acid hydrolysis - accomplished under the following preferred conditions, without the exclusion of any other:

- temperature range: 100°C-200°C;
- pressure above 2 atmospheres;
- acid used - sulfuric, hydrochloric or nitric, or their mixture;
- 25 - aqueous acid solution: 3% to 5% of acid, in weight;
- hydrolysis time: 30 minutes to 2 hours;
- ratio between weight of vegetal matter to weight of acid solution: 2:1 to 1:4.

During the hydrolysis potassium, sodium, calcium, magnesium and other inorganic impurities react with the acid forming, for instance, soluble sulfates with the sulfuric acid. Also during the hydrolysis the acid decomposes the hemicellulose.

5 When the process of the invention aims at obtaining basic oxides, the hydrolysis is a basic hydrolysis, and the preferred conditions remain the same, except that alkali is used instead of acid, and the preferred alkali are ammonium hydroxide, potassium hydroxide and sodium hydroxide, or their mixture.

10 B. Washing/drying

The resulting material from the hydrolysis is washed with water, in one or more operations aimed at this end, depending on the desired purity of the silica. One aims at the removal of soluble salts and the decomposed hemicellulose. One can use soft water - that is, with low salt content -,
15 distilled water or deionized water. The purity of the silica, as obtained at the end of the process depends on the efficiency of the soluble salt removal generated in the previous step, avoiding the presence of salts of basic character which later, during the step of calcination, form silicates that favor the sinterization of the silica - from this angle the use of hard water
20 is less adequate. Some preferential conditions during washing are as follows:

- the washing operation starts with potable water and ends with distilled or deionized water;
- the washing operation is performed until the pH of the resulting
25 waters is about 6;
- a larger number of washing actions with smaller amounts of water is preferred to a smaller number of washing actions with larger amounts of water.

At this stage one also performs, before going on to the next steps, the elimination of excess water from the washed material, for instance by filtration and/or drying, in any of the ways known to one skilled in the art.

It has been verified that the use of potable water provided silica with
5 BET specific area up to about $260\text{m}^2/\text{g}$, while the use of distilled or deionized water considerably increased such BET area to values above $480\text{m}^2/\text{g}$

BET (after Brunauer, Emmett e Teller) refers to a measure according the description by Paul A. Webb, P. A. and Orr, C, in *Analytical Methods in Fine Particle Technology*, edited by Micromeritics Instrument Corporation
10 (One Micromeritics Drive, Norcross, GA 30093, USA, ISBN 0-9656783-0-X).

C. Fragilization of the structure - this step aims at providing fragility to the obtained material, making its later disaggregation easy and efficient, also allowing the calcination temperature to be lower (compared to the absence of this step) as part of the organic material begins to decompose
15 here, under gaseous form. Such gases can be utilized as fuel in later steps of this process, for instance during calcination.

An efficient fragilization means is the exposure to heat between about 270°C and the temperature just below the flash point, or flame forming temperature of the vegetal matter from the prior step (ordinarily between
20 about 410°C and 430°C), for about two hours, or until a deep dark color is obtained , or until the material becomes brittle or easily breakable. Typically, the temperature of this step is about 320°C . The time necessary to perform this step depends of the husk heating process, being shorter when the husks are carried by a flux of hot air.

25 The fragilization step renders easier the later milling operation, and allows the use of lower temperatures during the later calcination operation (compared to the temperatures used in the absence of the step of fragilization).

D. Disaggregation - the material originated from the previous step can be easily disaggregated by any adequate physical, physico-chemical or chemical action. It is typically a mechanical operation, such a milling, advantageously under dry conditions. It was verified to be adequate, without excluding any alternative, a dry milling with 5mm diameter ceramic spheres, providing a fine powder with average diameter particle passable through a 325 mesh tamis or smaller. Also adequate are devices with mechanical or ultrasound vibrating means, crushing means, grinding means, or any equivalent means capable of performing disaggregation.

This disaggregation operation contributes to inhibit the aggregation of the silica in a later calcination step.

For some industries the resulting material from this step is useful, namely a composition essentially comprising carbon and silica, in a ratio of about 60:40. A example is the tire industry, as the rubber composition comonly comprises both carbon black and silica. This composition also finds uses in the cement industry, paint industry, etc.

Performing steps C and D sequentially is advantageous as they favor a finer particle size, compared to the alternative when one or the other is absent.

E. Calcination - it seeks to eliminate the organic part in the vegetal residue with the lowest possible temperatures, or with the shortest residence times of the dust in the calcination equipment. The higher the calcination temperature, the greater the undesired aggregation of the silica particles, mainly if alkaline or alkaline-terrous impurities are present. The preferred calcination temperature is between the flash point of the husk (between about 410°C and 430°C) and about 900°C, more specifically between about 440°C and 850°C, and more advantageously between 500°C and 650°C. An adequate form of calcination is the continuous burning of the

dust injected along with fuel in the flame of a blast burner or blowpipe, directed to the interior of the burning chamber to accomplish the burning in the shortest possible time. One aims at obtaining a white silica dust at the lowest possible temperature that is capable of eliminating all carbon; from another angle, when the final product is white, one knows that the organic content has been substantially eliminated. When one burns the material obtained according to the previous steps, one favors the direct provision of an amorphous silica dust of high specific area, low aggregation and low average particle size, of about 5 μ m.

Other adequate ways to perform the calcination is by using a fluidized bed oven, a rotary oven as the ones presently employed to burn ceramic dusts, a muffle type furnace with shallow crucibles, etc.

F. Milling - this step aims at providing the adequate finer particle size to the amorphous silica, as required to specific needs. It includes any operation that decreases the particle size obtained in the previous steps. It can be by wet means - for instance a ball mill with a deflocking agent - or by dry means, for instance by the chock of opposing jets, an impact rotary mill with particle size selection, a ball mill with continuous sweep of the fine fraction, etc.

One of the advantages of the process of the invention is, by comprising the steps of fragilization and disaggregation, permitting a lower use of energy during calcination, if compared to either the traditional direct burning of rice husks or to the process revealed by Real, Alcalá and Criado, previously mentioned. Furthermore, the use of higher pressures during the hydrolysis step permits a shortened hydrolysis time and the use of a lower acid content solution, favoring - or at least not decreasing - qualities such as purity, BET specific area and small particle size in the final product.

One of the processes of the invention is the one that comprises steps A, B, C, D and E described before, for obtaining high purity (above 99%) amorphous silica, with particle size between about 1 to 5 μm , high specific area above at least about 260 m^2/g , and high chemical reactivity.

5 Another process of the invention is the one that comprises steps A, B, C, D, E and F, through which one obtains amorphous silica with particle size below 1 μm .

Another process of the invention is the one that comprises alternatively steps A, B, C and E, or A, B, D and E, either one
10 optionally followed by step F, for obtaining high purity amorphous silica.

Another aspect of the invention is a high purity oxide, preferably silica, extracted from vegetal matter according to any of the processes mentioned hereinbefore.

15 Another process of the invention is the one that comprises steps A, B and C for obtaining carbon-rich oxide compositions, optionally followed by steps D and/or F.

Another aspects of the invention is compositions comprising essentially carbon and silica, obtained through a process according to steps
20 A, B and C, optionally followed by steps D and/or F.

Examples will now be given, only as illustrations of the invention, to facilitate its understanding.

Three batches identified as 1, 2 and 3, each with 30 kg of rice husks of different origins are subject to the following steps:

25 A. Hydrolysis

batches 1 and 2 – 4.5% sulfuric acid aqueous solution, using a 1:1 ratio between the weights of husks and acid solution, pressure of 5 atmospheres, temperature of 150°C, during 1 hour.

- batch 3 – 5% hydrochloric acid aqueous o, using a 1:1 ratio between the weights of husks and acid solution, pressure of 7 atmospheres, temperature of 170°C, during 2 hours.

B. Washing/drying

5 - batches 1 and 2 - potable water, in a container provided with filtration means, 30 liter portions for each washing action under agitation, until the resulting waters have a pH of about 6, followed by drying during 1 hour at 120°C in a muffle type oven.

- batch 3 – the same as for batches 1 and 2, including two extra 30 liter
10 distilled water washing actions.

C. Fragilization

- all batches – heating to 320°C during 60 minutes, with the material disposed in thin layers inside crucibles, in a muffle type oven.

D. Disaggregation

15 - all batches– dry milling in a rotary mill with 5mm diameter zirconia spheres, for 8 hours. The material obtained is a deep dark powder with average particle size below 44 µm.

E. Calcination

- batches 1 and 2 – temperature 550°C in a fluidized bed oven, residence
20 time 2 hours.

- batch 3 - temperature 500°C in a fluidized bed oven, residence time 2 hours.

F – Milling

-batches 1 and 2 – milling with 5 mm diameter zirconia spheres, in a wet
25 medium with 2% in weight of ammonium polyacrylate as deflocking agent, for 2 hours.

- batch 3 – same as with other batches, for 6 hours.

RESULTS

The table below shows the results:

Batch	color and % purity in SiO ₂	particle size (μm)	specific area (BET m ² /g)	(*) % average Pozolanicity
1 (before step F)	white, 99,2	5	260	90
1 (after step F)	white, 99,2	1	260	90
2	white, 99,6	0,8	280	90
3	white, 99,8	0,7	420	99

(*) According to the process described by Chapelle, J. in Revue de Matériaux de Construction, vol. 512, pages 136 and following, 1958, France.

CLAIMS

1. PROCESS FOR THE EXTRACTION OF OXIDES CONTAINED
IN VEGETAL MATTER, aiming at obtaining high purity oxides,
characterized by the fact that it comprises the following
steps:

A. Hydrolysis above 100°C, under pressure;

B. Washing/drying;

C. Fragilization of the structure;

D. Disaggregation of the structure;

E. Calcination;

2. PROCESS according to claim 1 characterized by the fact that it
comprises an additional final milling step.

3. PROCESS according to claim 1 characterized by the fact that it
comprises steps A, B, C and E, optionally followed by a final milling
step.

4. PROCESS according to claim 1 characterized by the fact that it
comprises steps A, B, D and E, optionally followed by a final milling
step.

5. PROCESS according to any of claims 1 to 4 characterized by the fact
that the hydrolysis step aims at obtaining acid oxides utilizing the
following conditions:

- temperature between about 100°C and e 200°C;

- pressure above 1 atmosphere;

- acid chosen from the group comprising sulfuric, hydrochloric and nitric
acids, or their mixture;

- acid concentration in water between about 3% and 5% in weight;

- ratio between the weights of vegetal matter and acid solution from
about 2:1 to about 1:4.

6. PROCESS according to any of claims 1 to 4 characterized by the fact that the hydrolysis step aims at obtaining basic oxides utilizing the following conditions:

- temperature between about 100°C and e 200°C;
- 5 - pressure above 1 atmosphere;
- alkali chosen from the group comprising ammonium hydroxide, potassium hydroxide and sodium hydroxide, or their mixture;
- alkali concentration in water between about 3% and 5% in weight;
- ratio between the weights of vegetal matter and basic solution from
10 about 2:1 to about 1:4.

7. PROCESS according to any of claims 1 to 6 characterized by the fact that said washing step B is performed with potable or soft water, distilled water or deionized water, until the resulting waters have a pH of about 6.

15 8. PROCESS according to any of claims 1, 2, 3, 5 or 6 characterized by the fact that said fragilization step C is performed by exposure to heat between about 270°C and the flame forming temperature or the flash point of the material, more adequately about 320°C, for up to about 2 hours.

20 9. PROCESS according to any of claims 1, 2 or 4 characterized by the fact that said disaggregation step D is a mechanical operation, preferably a dry milling operation.

10. PROCESS according to any of claims 1 to 4 characterized by the fact that said calcination step E is performed between the
25 flame forming temperature or the flash point of the material and about 900°C, preferably between about 440°C and about 850°C, more preferably between about 500°C and about 650°C.

11. PROCESS according to claim 10 characterized by the fact that said calcination is performed as a continuous burning of dust, injected along with fuel in the flame of a blast burner or blowpipe.

12. PROCESS FOR THE EXTRACTION OF OXIDES CONTAINED IN VEGETAL MATTER, aiming at obtaining carbon-rich oxide compositions, characterized by the fact that it comprises the following steps:

A. Hydrolysis above 100°C , under pressure;

B. Washing/drying;

C. Fragilization of the structure;

optionally followed by the steps of disaggregation of the fragilized material and/or milling.

13. PROCESS according to claim 12, aiming at obtaining carbon-rich acid oxide compositions, characterized by the fact that it utilizes the hydrolysis conditions of claim 5.

14. PROCESS according to claim 12, aiming at obtaining carbon-rich basic oxide compositions, characterized by the fact that it utilizes the hydrolysis conditions of claim 6.

15. PROCESS according to any of claims 12 and characterized by the fact that said washing step B utilizes the conditions of claim 7.

16. PROCESS according to claim 12 characterized by the fact that said fragilization step C utilizes the conditions of claim 8.

17. PROCESS according to claim 12 characterized by the fact that said optional disaggregation step utilizes the conditions of claim 9.

18. CARBON-RICH OXIDE COMPOSITIONS EXTRACTED FROM VEGETAL MATTER characterized by the fact that they are obtained by the process of any of the claims 12 to 17.

19. HIGH PURITY OXIDES EXTRACTED FROM VEGETAL MATTER characterized by the fact that they are obtained by the process of any of the claims 1 to 11.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/BR 01/00020

CLASSIFICATION OF SUBJECT MATTER

IPC⁷: C01B 13/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁷: C01B 13/18, C01B 33/12, C01B 33/20

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Questel WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	RU 2061656 (ASFA-R), 10 June 1996 (10.06.96), (abstract) WPI, London, UK: Derwent Publications Ltd., Questel/Orbit, Paris/France, DW 199709, Accession No.1997-098 538	1,5,19
A	CN 111 3216 A (WUGG-I), 13 December 1995 (13.12.95) (abstract), WPI, London, UK: Derwent Publications Ltd., Questel/Orbit, Paris/France, DW 199738, Accession No.1997 - 403 447	1,6,19
A	DD 276 671 (AKAD. WISSENSCHAFTEN DDR) 7 March 1990 (07.03.90) <i>claims.</i>	1,6,19
A	CN 1 229 057(JUFF-I) 22 September 1999 (22.09.99) (abstract) WPI, London, UK: Derwent Publications Ltd., Questel/Orbit, Paris/France, DW 1999, Accession No.1999-09-22	1,6,19

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

„A“ document defining the general state of the art which is not considered to be of particular relevance

„E“ earlier application or patent but published on or after the international filing date

„L“ document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

„O“ document referring to an oral disclosure, use, exhibition or other means

„I“ document published prior to the international filing date but later than the priority date claimed

„T“ later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

„X“ document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

„Y“ document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

„&“ document member of the same patent family

Date of the actual completion of the international search

29 November 2001 (29.11.2001)

Date of mailing of the international search report

17 January 2002 (17.01.2002)

Name and mailing address of the ISA/AT

Austrian Patent Office
Kohlmarkt 8-10; A-1014 Vienna

Facsimile No. 1/53424/535

Authorized officer

PAMMINGER

Telephone No. 1/53424/223

INTERNATIONAL SEARCH REPORT

International application No.
PCT/BR 01/00020

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 12-18
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

The claims 12-18 refer to the extraction of oxides contained in vegetal matter. It is not understandable in which way by the steps A. B. C. - comprising hydrolysing, washing and fragilisation - said oxides are extracted from vegetal matter.
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/BR 01/00020

Patent document cited in search report			Publication date	Patent family member(s)	Publication date
CN	A	1113216		none	
CN	A	1229057		none	
DD	A	276671		none	
RU	A	2061656		none	